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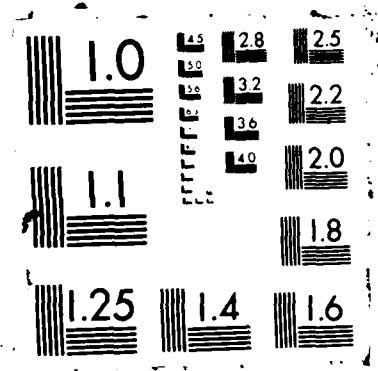
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Sehun Kim and R. Stanley Williams

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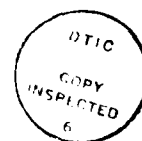
University of California, Los Angeles  
Department of Chemistry and Biochemistry  
and Solid State Sciences Center  
Los Angeles, CA 90024-1569

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Semiempirical band structure of PtGa<sub>2</sub>

Sehun Kim

*Department of Chemistry and Biochemistry and Solid State Sciences Center,  
University of California, Los Angeles, California 90024*

Li-Shing Hsu

*Department of Physics and Solid State Sciences Center, University of California, Los Angeles, California 90024*

R. Stanley Williams

*Department of Chemistry and Biochemistry and Solid State Sciences Center,  
University of California, Los Angeles, California 90024*

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A semiempirical band structure for PtGa<sub>2</sub> was obtained by adjusting the AuGa<sub>2</sub> parameters in the mixed-basis band-structure interpolation scheme to obtain agreement between the calculated total density of states (DOS) and x-ray photoemission spectroscopy data. Angle-resolved photoemission spectroscopy data collected from a PtGa<sub>2</sub> (111) surface with a noble-gas-discharge lamp as excitation source were used to check the energies of the *d* bands. The PtGa<sub>2</sub> band structure is compared to those of both elemental Pt and Au, and the gold color of PtGa<sub>2</sub> is explained in terms of its Au-like DOS.

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## I. INTRODUCTION

The study of the electronic structure of materials has been an intense field of research in the past two decades. During this time the experimental theoretical methods available have become increasingly sophisticated. Elemental metal such as Ag have been examined in great detail, and the agreement between recent band-structure calculations<sup>1</sup> and angle-resolved photoelectron spectroscopy (ARPES) data<sup>2</sup> for this system is excellent. However, determining the band structure of a compound is far more challenging. The increased number of atoms in the primitive unit cell makes *ab initio* calculations much more difficult, and there are thousands of compounds (mostly intermetallic compound) composed of just two elements. The likelihood that a band structure has been calculated for an arbitrary compound is very small, and thus reliance on experimental determinations and semiempirical calculations of valence-band structures will probably increase as the materials community investigates new classes of compounds.

Binary intermetallic compounds that contain a transition metal and a group-III metal are interesting from both technological and academic points of view. For instance, conducting contacts of AuGa<sub>2</sub> are thermodynamically more stable than elemental Au on GaSb (Ref. 3) and GaAs (Ref. 4), and thus the electronic and magnetic properties of this and related intermetallic compounds may be important in circuitry. Such compounds are also excellent systems for studying *d* bands, since the group-III metals contribute only *s-p* states to the valence band. This makes it possible to examine the effects of structure and chemical bonding on *d* states in the compounds. The primary concern of this paper is the effect of the Ga

valence states on the *d* states of Pt in PtGa<sub>2</sub>.

The only *ab initio* band structures for compounds similar to PtGa<sub>2</sub> are those for the structurally related compounds AuAl<sub>2</sub>, AuGa<sub>2</sub>, and AuIn<sub>2</sub>, which were calculated by Switendick and Narath<sup>5</sup> in 1968. That calculation ignored spin-orbit splitting effects and used a rather small basis set. We have recently refined Switendick's band structures of AuGa<sub>2</sub> and AuIn<sub>2</sub> by the use of a combination of data from x-ray photoelectron spectroscopy (XPS) (Ref. 6) and ARPES (Ref. 7) to revise the parameters that were initially fitted to the *ab initio* band structures in a mixed-basis band-structure interpolation scheme (MBBSIS).<sup>8</sup> The MBBSIS, which was based on that developed by Smith,<sup>9</sup> may then be used to compute the full *E* versus *k* dispersion relations for the bands, calculate total or orbital-symmetry-projected density of states (DOS),<sup>10</sup> or even plot out approximate charge densities<sup>11</sup> to obtain a bond picture of the compounds.

Several interesting features were noted in the semiempirical band structures of AuGa<sub>2</sub> and AuIn<sub>2</sub>.<sup>7,8</sup> The apparent width of the *d* bands of the two compounds was narrower than those of elemental Au, even though the relative splitting of the three *d* states at  $\Gamma$  of the Brillouin zone (BZ) for Au, AuGa<sub>2</sub>, and AuIn<sub>2</sub> was nearly identical. Thus the crystal-field effects appeared to be similar for all three materials; the narrowing of the *d* bands of the intermetallic compounds resulted primarily from the fact that they appeared in a band gap of the *s-p* states and thus hybridized only weakly with strongly dispersing bands.

The present study of the valence bands of PtGa<sub>2</sub> was initiated to gain additional insight into the *d*-band structure of intermetallic compounds. The crystal structure of PtGa<sub>2</sub> is cubic fluorite, the same as AuGa<sub>2</sub> and AuIn<sub>2</sub>, and the lattice constant is 5.911 Å, which is slightly

smaller than that of  $\text{AuGa}_2$  ( $6.063 \text{ \AA}$ ).<sup>12</sup>  $\text{PtGa}_2$  is a gold-colored compound, so its electronic structure should resemble that of Au. No previous band structure of  $\text{PtGa}_2$  existed, so the MBBSIS band structure of  $\text{AuGa}_2$  was adjusted to provide agreement between the MBBSIS DOS and XPS data for  $\text{PtGa}_2$ . ARPES data collected from a  $\text{PtGa}_2$  (111) surface with a noble-gas-discharge lamp as the excitation source were used to check the energies of the  $d$  bands.

Section II of this paper describes the experimental procedure. In Sec. III the experimental data and the semiempirical band structure are presented and discussed. The conclusions of this work are contained in Sec. IV.

## II. EXPERIMENTAL PROCEDURE

A single crystal<sup>13</sup> of  $\text{PtGa}_2$  was oriented using Laue x-ray diffractometry, and then was cut by a wire saw to reveal a (111) surface. The  $\text{PtGa}_2$  sample was mounted on a polishing fixture, reoriented to within  $1^\circ$  of the (111) plane by Laue photography, and polished to mirror smoothness using 0.5-, 0.3-, and 0.05-mm alumina grit. The crystal was etched for about two minutes in *aqua regia*, and degreased with acetone and methanol before it was mounted in either the XPS or the ARPES chambers.

The XPS data for  $\text{PtGa}_2$  were collected with a vacuum generators Escalab equipped with a nonmonochromatic  $\text{Mg K}\alpha$  ( $h\nu = 1253.6 \text{ eV}$ ) x-ray source. The sample was cleaned by several cycles of sputtering with Ar ions and annealing until the XPS spectra showed that the O and C contamination of the surface was negligible. The valence-band spectra were collected overnight, and subsequent core-level spectra showed that the surface contamination during the data accumulation was also negligible. Since low-energy electron diffraction (LEED) and Auger measurements were not available in the present ARPES chamber for this experimental, a cleaning procedure similar to that described above was used. Alternating cycles of argon-ion bombardment and annealing to 825 K were done for two days, and a final cleaning cycle was performed just prior to data acquisition. The ARPES spectra were free of any obvious contamination by O or C, but the spectra were broad and contained contributions from several different emission lines. These proved to be a major nuisance, since intense emission from the Ga  $3d$  states, photoexcited by a high-energy satellite, often interfered with the valence spectrum corresponding to one of the primary emission lines.

The photoelectrons were collected with a  $160^\circ$  hemispherical electrostatic energy analyzer. The noble-gas-discharge lamp was operated with He, Ne, and Ar to provide various photo energies (Ar I, 11.6; Ne I, 16.9; Ne II, 26.9; He I, 21.2; and He II, 40.8 eV). The angle of incidence of the light with respect to the sample surface was  $52.5^\circ$ . Typical photoelectron intensities at normal emission for most of the lines were about  $2 \times 10^4$  counts/sec except for the He II line, for which the count rate was  $6 \times 10^2$  counts/sec. The analyzer was operated in a constant-pass energy mode with a resolution of approximately 0.3 eV.

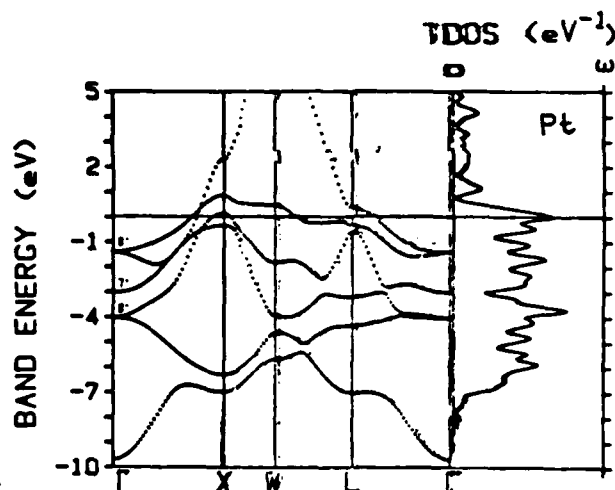


FIG. 1. Band structure and TDOS of Pt calculated using the 16-plane-wave MBBSIS. The parameters were fitted to the first-principles calculation of Ref. 14. The energy scale is referenced to the Fermi energy and the TDOS scale is in electrons of two spins per eV per unit cell volume.

## III. RESULTS AND DISCUSSION

The energy bands and total DOS (TDOS), calculated using Smith's interpolation scheme with 16 plane waves in the basis set, are presented for Pt and Au in Figs. 1 and 2, respectively, for comparison with those of  $\text{PtGa}_2$ . Although the parameters for Smith's previous interpolation scheme, with 4 plane waves in the basis set, were available for Pt from Ref. 14, they were revised to be consistent with the 16-plane-wave interpolation scheme. The band structure of Pt in Fig. 1 was obtained by fitting the MBBSIS parameters to the first-principles calculation of Anderson,<sup>15</sup> which agreed very well with the ARPES data of Ref. 16. The spin-orbit parameter ( $\zeta = 0.59$ ),<sup>16</sup> determined from the splittings of the  $d$  bands at  $\Gamma$  from the first-principles calculation of Anderson,<sup>17</sup> was used for Pt

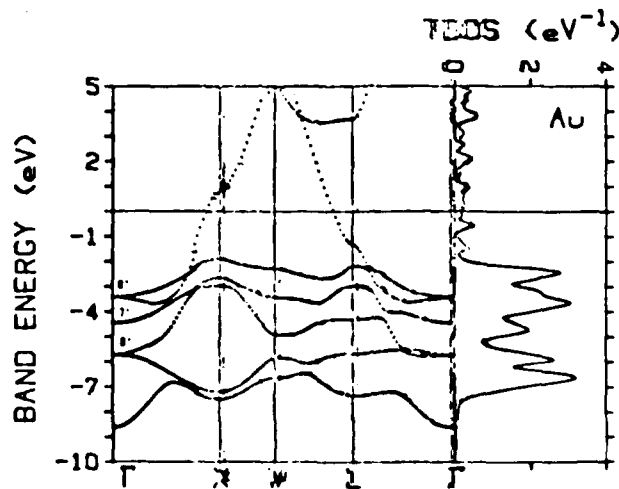


FIG. 2. Band structure and TDOS of Au calculated using the 16-plane-wave MBBSIS and the parameters of Ref. 9.

to provide a more precise agreement with Anderson's band structure. The Au band structure in Fig. 2 was calculated using the MBBSIS parameters published in Ref. 9. Figure 3 is the semiempirical band structure of PtGa<sub>2</sub>, which was obtained by adjusting the MBBSIS parameters<sup>8</sup> of AuGa<sub>2</sub> to optimize the agreement between the calculated total DOS and the XPS valence-band spectra for PtGa<sub>2</sub>, as shown in Fig. 4. The experimental value for the spin-orbit parameter for elemental Pt ( $\xi=0.63$  eV) (Ref. 14) was used in the MBBSIS for PtGa<sub>2</sub>, since Ref. 7 showed that  $\xi$  for Au was nearly the same in both the elemental metal and in the intermetallic compounds AuGa<sub>2</sub> and AuIn<sub>2</sub>.

Table I lists the MBBSIS parameters used to generate the energy bands and TDOS for Pt and PtGa<sub>2</sub>. The MBBSIS with 16 plane waves in the basis set was used for the Pt energy bands, while the version with 39 plane waves was used for PtGa<sub>2</sub>. Thus a direct comparison between Pt and PtGa<sub>2</sub> pseudopotential parameters may not be meaningful. However, the smaller values of the hy-

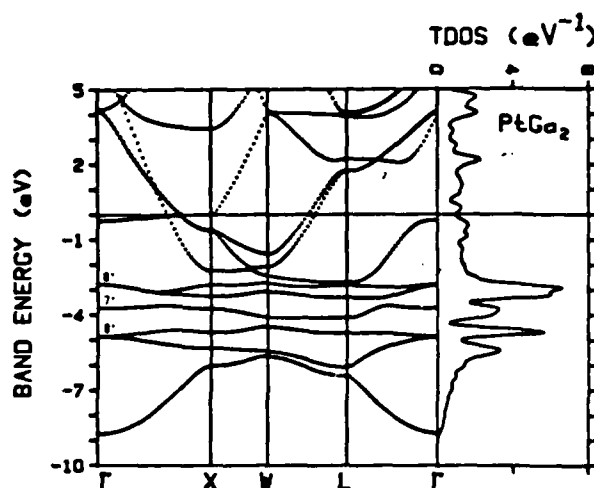


FIG. 3. Band structure and TDOS of PtGa<sub>2</sub>. The 39 plane-wave MBBSIS parameters for AuGa<sub>2</sub> of Ref. 8 were adjusted to improve the agreement between the calculated TDOS and the XPS valence-band spectrum of PtGa<sub>2</sub>.

TABLE I. MBBSIS parameters for Pt and PtGa<sub>2</sub> band structures. All values in eV except  $R$  in a reduced unit ( $4a/\pi$ ) and the lattice constant in Å. The  $\pm$  signs indicate the standard deviation of parameters. The parameters are intentionally reported with more significant figures than justified by the standard deviations in order to produce band structures that are essentially identical with those shown in Figs. 1-3. The MBBSIS employed for the Au and Pt band structures utilized 16 plane waves in the basis set, while that for PtGa<sub>2</sub> used 39 plane waves.

Parameters	Pt <sup>a</sup>	PtGa <sub>2</sub> <sup>b</sup>
$E_0$	$8.368 \pm 0.2$	$2.288 \pm 0.2$
$\Delta$	$0.1334 \pm 0.4$	$-0.2868 \pm 0.5$
$A_1$	$0.2383 \pm 0.1$	$0.0423 \pm 0.1$
$A_2$	$0.0137 \pm 0.07$	$-0.0119 \pm 0.07$
$A_3$	$-0.0556 \pm 0.1$	$0.0570 \pm 0.2$
$A_4$	$-0.0419 \pm 0.1$	$0.0561 \pm 0.1$
$A_5$	$0.0413 \pm 0.08$	$-0.0507 \pm 0.08$
$A_6$	$0.1283 \pm 0.1$	$0.0373 \pm 0.1$
$S$	$8.21 \pm 6$	$6.68 \pm 2$
$B_1$	$36.99 \pm 2$	$8.42 \pm 2$
$B_2$	$37.45 \pm 3$	$4.56 \pm 5$
$\alpha$	$0.2008 \pm 0.004$	$0.0607 \pm 0.001$
$R$	$0.3127 \pm 0.01$	$0.2535 \pm 0.02$
$V_{000}$	$-0.7663 \pm 0.3$	$0.1424 \pm 0.2$
$V_{111}$	$0.0123 \pm 0.4$	$2.564 \pm 0.2$
$V_{200}$	$0.5956 \pm 0.6$	$3.707 \pm 0.2$
$V_{220}$	$3.946 \pm 0.6$	$1.972 \pm 0.2$
$V_{311}$	$2.402 \pm 0.6$	$1.769 \pm 0.2$
$V_{222}$	$2.565 \pm 0.6$	$1.275 \pm 0.3$
$\xi$	0.59	0.63
$E_F^c$	8.90	5.55
Lattice constants	3.92	5.911
Average deviation	0.15	d

<sup>a</sup>Parameters were fitted to first-principles results of Ref. 15 using 16 plane waves in the basis set. The spin-orbit parameter  $\xi$  was taken from Ref. 16.

<sup>b</sup>Parameters were empirically adjusted to improve the agreement between the calculated total DOS and XPS data. The experimental value of the spin-orbit parameter  $\xi$  of Pt taken from Ref. 14 was used for that of PtGa<sub>2</sub>.

<sup>c</sup>Taken from Ref. 14 for Pt. The value for PtGa<sub>2</sub> was determined from the DOS calculation. These offsets are used to define the Fermi energy as the zero of the energy scale for each band structure.

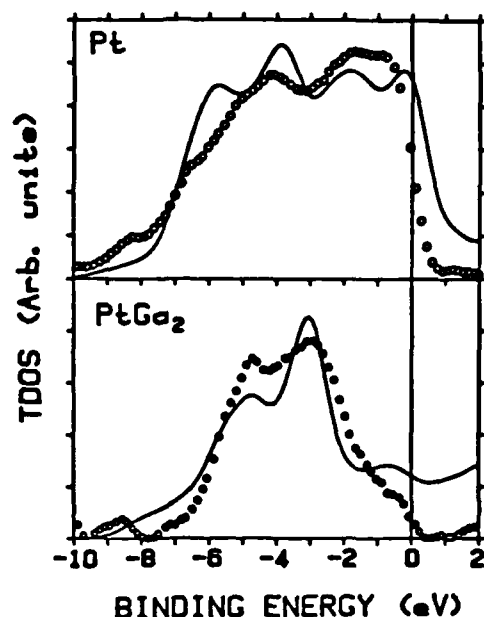


FIG. 4. Comparison between the XPS spectra (circles) with a piecewise linear background subtracted and the calculated TDOS (solid line) with 1.0 eV Gaussian broadening for Pt and PtGa<sub>2</sub>. The curves are plotted vs binding energy referenced to the Fermi energy. The calculated curve shows both the occupied and unoccupied DOS. There is a striking similarity between the XPS valence-band spectra of PtGa<sub>2</sub> and Au.

bridization parameters  $B_1$  and  $B_2$  of PtGa<sub>2</sub> compared to those of Au and Pt indicate less hybridization of the  $d$  bands with the other bands, as observed previously in the case of the Au intermetallic compounds.<sup>8</sup>

In the earlier study<sup>7</sup> of Au, AuGa<sub>2</sub>, and AuIn<sub>2</sub>, the width of the  $d$  density of states for the Au intermetallic compounds was much narrower than for elemental Au, even though the  $d$  band splitting at  $\Gamma$  was nearly identical for all three materials. This was taken as evidence that the crystal-field effects were similar in all three materials, despite the fact that the Au-Au distance varied drastically. The narrowing of the  $d$  bands of the compounds resulted primarily from the fact that they reside within a band gap of the  $s-p$  bands and thus hybridize only weakly with the highly dispersing bands. By comparing energy bands and TDOS for Pt and PtGa<sub>2</sub> in Figs. 1 and 3, one can see that the  $d$  band splitting at  $\Gamma$  for Pt (2.7 eV) is 35% larger than for PtGa<sub>2</sub> (2.1 eV), and thus there appears to be some effect of the Pt-Pt distances on the relative widths of the  $d$  bands in Pt and PtGa<sub>2</sub>. The total  $d$ -band width for elemental Pt is twice that of PtGa<sub>2</sub>, however, as can be seen in the comparison of the XPS valence-band spectra and TDOS calculations in Fig. 4. For a more complete discussion of the difference contributions to the total bandwidth, see Ref. 8. The same reasoning discussed for Au and AuGa<sub>2</sub> can be applied to the case of Pt and PtGa<sub>2</sub>. The dimensions of the BZ for PtGa<sub>2</sub> are smaller than for Pt, since the lattice constant of PtGa<sub>2</sub> is much larger than that of Pt. Thus the strongly dispersing  $s-p$  band reaches the BZ boundary before it can cross the  $5d$  bands, as shown in Fig. 3. Therefore, the  $d$

bands of PtGa<sub>2</sub> appear in a band gap of the  $s-p$  band<sup>5</sup> and hybridize only weakly with the strongly dispersing bands, while elemental Pt  $d$  bands mix strongly with an  $s-p$  band and create a broad TDOS.

An XPS valence-band spectrum represents an experimental density of states of the valence bands that is weighted by the photoionization cross sections of the various components within the valence band. Thus XPS spectra can be used to test band-structure calculations. In Fig. 4 the XPS spectra of Pt and PtGa<sub>2</sub> are compared with the TDOS calculated by the MBBSIS. The TDOS was calculated at 60 special  $k$  points<sup>18</sup> with a 1.0-eV Gaussian broadening to simulate the experimental resolutions and intrinsic broadening effects. The agreement between the TDOS calculations and the XPS spectra is reasonably good, except for the relative intensities of the features in the spectra. The first peak at -3 eV in the calculated TDOS of PtGa<sub>2</sub> shows a higher density of states than the second peak at -5 eV, while the two peaks in the XPS spectrum are comparable. This probably results from the fact that the upper three  $d$  bands of  $\Gamma_8$  and  $\Gamma_7$  symmetry are flat bands in the MBBSIS, and show less dispersion across the BZ than that of the lower two  $d$  bands of  $\Gamma_8$  symmetry. The small feature at -8.5 eV in the XPS spectrum was caused by the Mg  $K\alpha_{3,4}$  satellite x-ray line. The bandwidth at half maximum of the XPS spectrum for PtGa<sub>2</sub> (3.9 eV) was larger than for AuGa<sub>2</sub> (3.2 eV).<sup>8</sup>

Figure 5 presents the normal-emission ARPES spectra of the PtGa<sub>2</sub> (111) surface at different photon energies us-

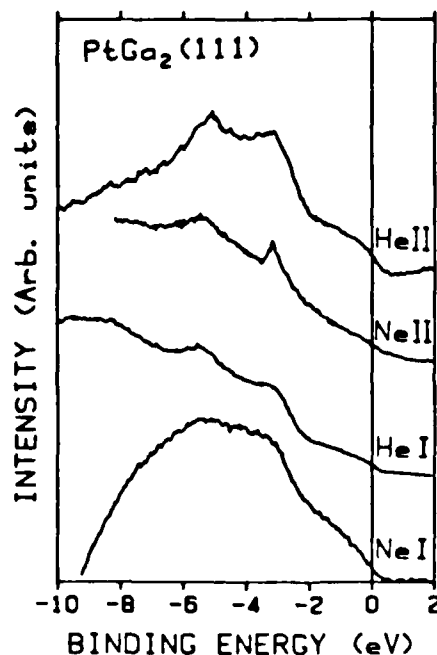


FIG. 5. ARPES spectra at normal emission for PtGa<sub>2</sub> (111) collected using a noble-gas-discharge lamp as the excitation source. The two primary features observed in each spectrum correspond to the two  $\Gamma_8$  bands of PtGa<sub>2</sub>, and essentially no dispersion of these two bands across the  $A$  direction of the BZ is detected, in agreement with the band structure of Fig. 3.



ing a noble-gas-discharge lamp as the excitation source. The ARPES spectra of PtGa<sub>2</sub> reveal two broad peaks, which arise from the Pt 5-*d* bands, that show little dispersion and confirm that the *d* band splitting at  $\Gamma$  is 2.1 eV. The spectra taken with He I and Ne I radiation are even broader than the He II and Ne II spectra, because of the contribution of the inelastic scattering tail. The ARPES spectra do not reveal any features other than the two peaks already observed in the XPS spectrum, even though the resolution was much better. The middle *d* band of PtGa<sub>2</sub> ( $\Gamma_7$ ) in Fig. 3, which is flat along the high-symmetry line in the BZ, was not resolved in the ARPES spectra. In the case of AuGa<sub>2</sub>, the middle *d* band was observed in ARPES spectra for photon energies below 26 eV.<sup>7</sup> The corresponding feature from the flat middle *d* band of PtGa<sub>2</sub> was not apparent in the He I (21.2 eV) and Ne I (16.9 eV) spectra, perhaps because of increased lifetime broadening effects or the fact that the *d* bands are energetically closer together at  $\Gamma$  in PtGa<sub>2</sub> than in AuGa<sub>2</sub>.

The band structures of Figs. 1–3 show why Pt is silver colored and PtGa<sub>2</sub> is gold colored. The Pt DOS is relatively high across the entire region from 1 to 4 eV binding energy, so that the absorption of light by Pt is fairly constant over the entire visible range of the electromagnetic spectrum. For Au and PtGa<sub>2</sub>, however, an *s-p* plateau with a fairly low DOS extends from 0–2 eV binding energy, whereas at higher binding energies there is a very high *d* DOS. Thus the PtGa<sub>2</sub> DOS looks very similar to that of Au, and their color arises from the fact that blue and violet light are absorbed much more strongly than yellow and red light. The shape of the PtGa<sub>2</sub> DOS can be understood by considering the fact that elemental Ga has a

work function of 4.2 eV<sup>19</sup> whereas that for Pt is 5.7 eV.<sup>19</sup> Adding the *s-p* DOS of Ga to the Pt DOS, with the vacuum levels of the two elements in common, would yield a picture qualitatively similar to the PtGa<sub>2</sub> DOS in Fig. 3. Since the Pt *d* states are below the Fermi level of the compound, they are completely filled, and the total *d* band width of the compound is narrower than that for elemental Pt for the reasons discussed previously.

#### IV. CONCLUSIONS

A semiempirical band structure of PtGa<sub>2</sub> was obtained by adjusting the MBBSIS parameters of AuGa<sub>2</sub> to improve the agreement between the calculated total DOS and XPS data for PtGa<sub>2</sub>. The *d*-band width of PtGa<sub>2</sub> was much narrower than that of Pt, since the *d* bands reside in a band gap of the *s-p* bands and thus hybridize weakly with the *s-p* bands. The gold color PtGa<sub>2</sub> arises from the preferential absorption of blue and violet light caused by the abrupt increase of the DOS at a binding energy of 2 eV, which is also a feature of the Au DOS.

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